

## Uranium speciation impacts isotope signatures arising from microbial U(VI) reduction

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Microbial reduction of U(VI) is widespread in the environment, both in pristine and engineered environments. Several studies have shown that such enzymatic redox transformations are accompanied by mass-independent isotope fractionation, with enrichment of the heavy U-238 in the U(IV) products, in accordance with nuclear field shift theory. However, fundamental mechanistic information is lacking on the factors that affect the direction and magnitude of the U isotope signature.

To address the importance of uranium speciation during reduction by the model bacterium *Shewanella oneidensis* MR-1, we systematically varied medium composition to impact U(VI) and U(IV) solubilities and reduction kinetics.

First, we show that the formation of soluble ternary calcium-uranyl-carbonate results in enhanced isotope fractionation, compared to uranyl-carbonate species, and is possibly related to slower reduction kinetics. Second, the enzymatic reduction of a novel insoluble U(VI)-organic ligand complex (U-DPAEA) to a stable, soluble U(V) product resulted in negligible isotope fractionation. This suggests that preferential reduction of the heavier isotope, observed previously, may be associated with the second electron transfer, rather than the first one-electron transfer observed here. Third, precipitation of U(VI) with phosphate significantly suppressed the rate of reduction to insoluble U(IV) species and we hypothesise that phosphate limits the availability of uranium isotopes to undergo equilibrium isotopic exchange. The isotopic fractionation in this system is currently under investigation.

These data provide the first steps toward a comprehensive understanding of microbial signatures of uranium isotope fractionation in both ancient and modern rocks and sediments.